
An open-framework boron allotrope exhibiting high conductivity and plasticity

In the format provided by the
authors and unedited

Outline:

1. Theoretical assessment of alkali-metal removal from borides

2. Nucleation-mitigation effect of a zinc interlayer during synthesis of Na_4B_{60} crystals

3. X-ray diffraction analysis for structural characterization of Na_4B_{60} and B_{60}

4. Elemental analysis for B_{60} via energy-dispersive spectroscopy (EDS) to determine residual Na content

5. Thermodynamic and dynamic stability of *Imma*- B_{60}

6. Electron diffraction of *Imma*- B_{60}

7. Structural comparison between *Imma*- B_{60} and other synthesized boron allotropes

8. Chemical bonding analysis of *Imma*- B_{60}

9. Electronic transport properties of Na_4B_{60} and B_{60}

10. Optical adsorption and optical bandgap of Na_4B_{60} and B_{60}

11. Calculated band structures of *Imma*- Na_4B_{60} and *Imma*- B_{60}

12. In-situ uniaxial compression data of B_{60} and Na_4B_{60}

1. Theoretical assessment of alkali-metal removal from borides

Fundamentally, boron possesses only three valence electrons, making it electron-deficient when forming covalent framework. This leads to unique multicenter bonding and a strong thermodynamic drive to combine with electron-donating metal atoms. These intrinsic properties cause two major obstacles to applying the precursor-degassing methodology for synthesizing new boron allotropes. First, the stronger boron-metal bonds require substantially larger energy to break. As quantified in Supplementary Table 1, the calculated Bader charge transfer¹ and formation energies for alkali metals in three candidate borides with open channels are significantly larger than those in Na₄Si₂₄, indicating the difficulty of extracting alkali metals from these boride precursors. Second, the structural integrity of the boron framework after alkali-metal removal is not guaranteed. Boron's versatile multicenter bonding enables facile structural relaxation through flexible re-bonding, which often leads to phase collapse or transition. The conversion of Na₃B₂₀ into Na₄B₆₀ at elevated temperatures due to the sodium loss exemplifies this inherent tendency. Identifying a boride precursor that is both stable and capable of retaining its framework after metal removal thus requires a delicate balance. Notably, as shown in Supplementary Table 1, the Na-B interaction in Na₄B₆₀ is relatively weak among the borides considered. This played a key role in enabling the successful synthesis of *Imma*-B₆₀.

Supplementary Table 1 | Formation energies and Bader charge transfer for alkali-metal atoms in representative channel-containing compounds. Formation energy of alkali-metal element *A* in *A_xB_y* compounds is calculated by: $E_f = [E(B_y) + xE(A) - E(A_xB_y)]/x$, where $E(A)$ is the energy of a single *A* atom, and $E(B_y)$ is the energy of metal-free covalent framework.

Structure	<i>Cmcm</i> -Na ₄ Si ₂₄	<i>P4/mbm</i> -LiB ₃	<i>Cmmm</i> -Na ₃ B ₂₀	<i>Imma</i> -Na ₄ B ₆₀
Formation energy (eV)	1.7	4.4	3.8	3.4
Charge of alkali metal atom (<i>e</i>)	0.80	0.88	0.86	0.84

2. Nucleation-mitigation effect of a zinc interlayer during synthesis of Na₄B₆₀ crystals

Given the low mutual solubility between zinc and both boron and sodium^{2,3}, a zinc interlayer was strategically employed during high-pressure synthesis (Extended Data Fig. 1a). In this configuration, the zinc interlayer is placed between the boron and sodium layers. This design suppresses excessive nucleation at the boron-sodium interface and effectively promotes the growth of Na₄B₆₀ single crystals, yielding significantly larger crystals than previously reported⁴ (Extended Data Fig. 1b). To unambiguously confirm the role of the zinc interlayer, a control experiment was performed with the zinc layer placed outermost while all other conditions remained unchanged (Extended Data Fig. 1d). The resulting crystals were generally smaller in the absence of the zinc interlayer (Extended Data Fig. 1e). By measuring the dimensions of 292 crystals from the assembly with the interlayer and 341 crystals from the control configuration, a statistical comparison is presented in Extended Data Fig. 1c,f. The assemble with the zinc interlayer produced crystals mostly in the 100–300 μm range, whereas the control assemble yielded crystals predominantly under 80 μm . The larger, high-quality single crystals obtained with the zinc interlayer enabled more accurate structural determination and more reliable measurements of key properties such as electrical resistivity and hardness.

3. X-ray diffraction analysis for structural characterization of Na₄B₆₀ and B₆₀

Four single-crystal diffraction datasets were collected from three samples (S1–S3). The structure of Na-B crystal was refined using 338 (S1-1) and 447 (S1-2, S2, S3) unique reflections against 45 refined parameters. Key results are summarized in Supplementary Tables 2 and 3. All four independent refinements converged to the same structural solution presented in Extended Data Table 1 (also see the separate crystal structure file on the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2487320), and show consistent residual-density distributions and thermal-displacement parameters (Supplementary Table 4). These results confirm that the *Imma*-Na₄B₆₀ model reliably describes the synthesized single crystals and demonstrate the reproducibility of our results.

A close inspection of the refinements revealed that several weak peaks in the powder XRD patterns (indicated by black arrows in Fig. 1c) are not accounted for the ideal *Imma*-Na₄B₆₀ and *Imma*-B₆₀ structures. Furthermore, single-crystal diffraction shows residual density peaks (q1 and q2 in Supplementary Table 3) and a relatively large thermal displacement parameter for the B6 atoms (Supplementary Table 4 and Extended Data Fig. 5a,b). Since both the enhanced thermal displacement and the residual density coincide with interstitial boron sites, we propose two defect models involving positional modulation of the interstitial B atoms to explain the additional reflections. In defect structure I, the B6 atom is displaced to the position of residual density peak q1 (Extended Data Fig. 5e,f), while defect structure II is constructed by rotating a B5-B6 pair into the region associated with large thermal displacement and residual density peak q2 (Extended Data Fig. 5g,h). Both models were fully relaxed using DFT calculations to verify their stability, and the optimized structures were subsequently employed to simulate powder XRD patterns. Strikingly, the weak reflections near 17.5°, 22.8°, 29.9°, and 31.7° in the Na₄B₆₀ XRD patterns (Extended Data Fig. 5i–k), and those near 17.5°, 20.5°, 30.3°, and 38.6° in the B₆₀ patterns (Extended Data Fig. 5l–n), are consistently reproduced by these defect models. This indicates that the same boron framework and defect types persist in the crystals before and after Na-removal. It should be noted that not all predicted defect-related reflections are visible in the experimental patterns, and some exhibit slight shifts or broadening relative to the simulations, which are likely due to limited long-range order of the defects and associated

local lattice distortions. In contrast, the reflections arising from the ideal *Imma* structure remain complete, sharp, and intense in the experimental data, confirming the *Imma* structure as the foundational crystal model for these samples.

Supplementary Table 2 | Structure refinement parameters (S1-1) for Na₄B₆₀ determined using laboratory X-ray diffraction data

Crystal data	
Chemical formula	NaB ₁₅
Crystal system	orthorhombic
Space group	<i>Imma</i>
<i>a</i> , <i>b</i> , <i>c</i> /Å	5.8466 (8), 10.3770 (14), 8.3187(11)
α , β , γ /°	90, 90, 90
<i>V</i> /Å ³	504.70 (12)
<i>Z</i>	4
Intensity measurement	
Diffractometer	Bruker D8 Venture Photon 100 COMS
<i>T</i> _{meas} /K	300(2)
Radiation	Mo- <i>K</i> α, λ = 0.71073 (Å)
Scan mode	φ and ω scan
Time per step /s	2
Absorption correction	Multi-scan
<i>F</i> (000)	344
θ range /°	3.93-27.47
μ /mm ⁻¹	0.171
Refinement of the structure	
No. measured reflections	6314
No. unique reflections	338
No. observed reflections(<i>I</i> > 2σ(<i>I</i>))	311
No. reflections used in refinement	338
No. parameters used in refinement	45
Reflection range	-7 ≤ <i>h</i> ≤ 7, -13 ≤ <i>k</i> ≤ 13, -10 ≤ <i>l</i> ≤ 10
<i>R</i> _{int}	0.0862
<i>R</i> (σ)	0.0261
Final <i>R</i> indices (<i>F</i> _{obs} > 4σ(<i>F</i> _{obs}))	<i>R</i> ₁ = 0.0618, ωR_2 = 0.1314
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0675, ωR_2 = 0.1314
Goodness of fit	1.157

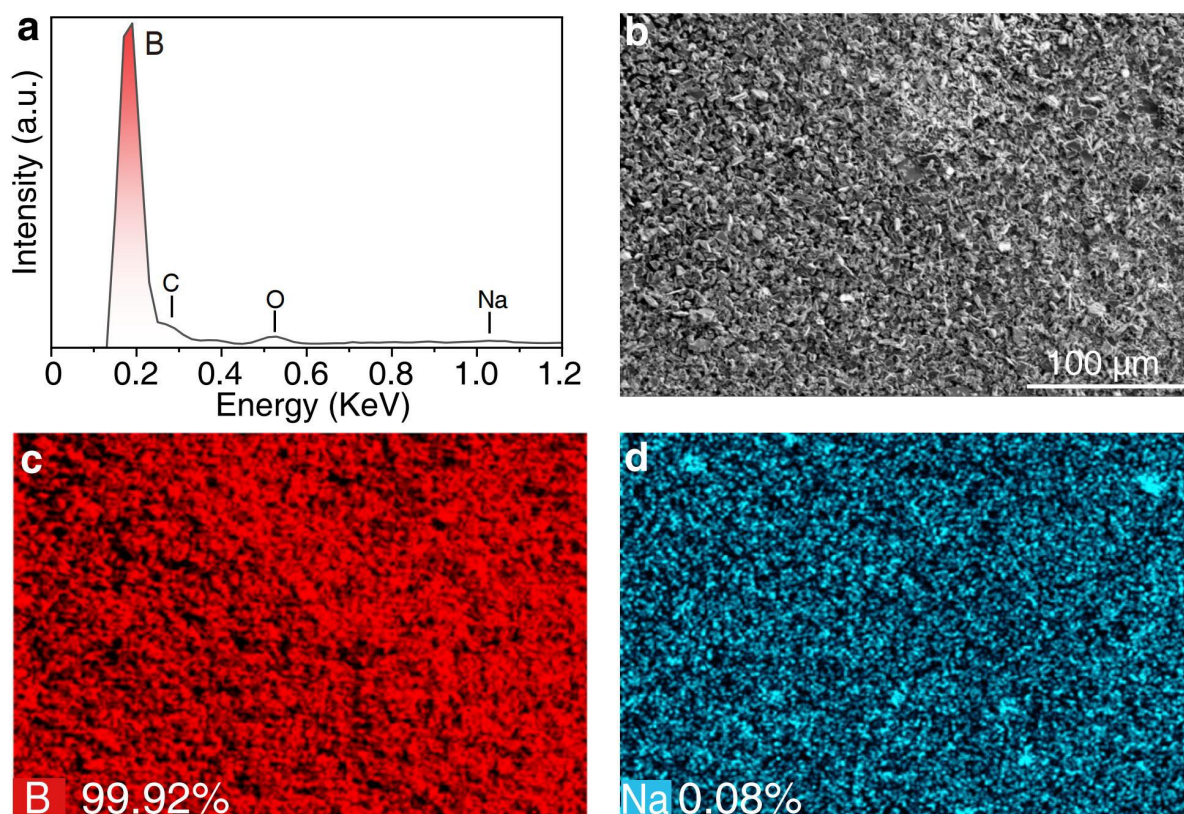
Supplementary Table 3 | Summary of single-crystal XRD refinement statistics for *Imma*-Na₄B₆₀ from independent crystals (S1–S3).

Experiment	reflection-to-parameter ratio	<i>R</i> -factors	Residual density (<i>e</i> Å ⁻³)	
S1-1	7.5	<i>R</i> _{int} =8.62 %	(0.2500,0.1037,0.2500)	q ₁ =1.00
		<i>R</i> ₁ =6.18 %	(0.3513,0.2004,0.2002)	q ₂ =0.54
S1-2	9.9	<i>R</i> _{int} =6.86 %	(0.2500,0.1019,0.2500)	q ₁ =1.12
		<i>R</i> ₁ =6.97 %	(0.3597,0.2041,0.2031)	q ₂ =0.74
S2	9.9	<i>R</i> _{int} =5.17 %	(0.2500,0.1035,0.2500)	q ₁ =1.18
		<i>R</i> ₁ =6.00 %	(0.3585,0.2017,0.2032)	q ₂ =0.75
S3	9.9	<i>R</i> _{int} =4.76 %	(0.2500,0.1025,0.2500)	q ₁ =1.15
		<i>R</i> ₁ =6.08 %	(0.3609,0.2054,0.1985)	q ₂ =0.66

Supplementary Table 4 | Anisotropic displacement parameters for *Imma*-Na₄B₆₀ derived from single-crystal XRD refinement.

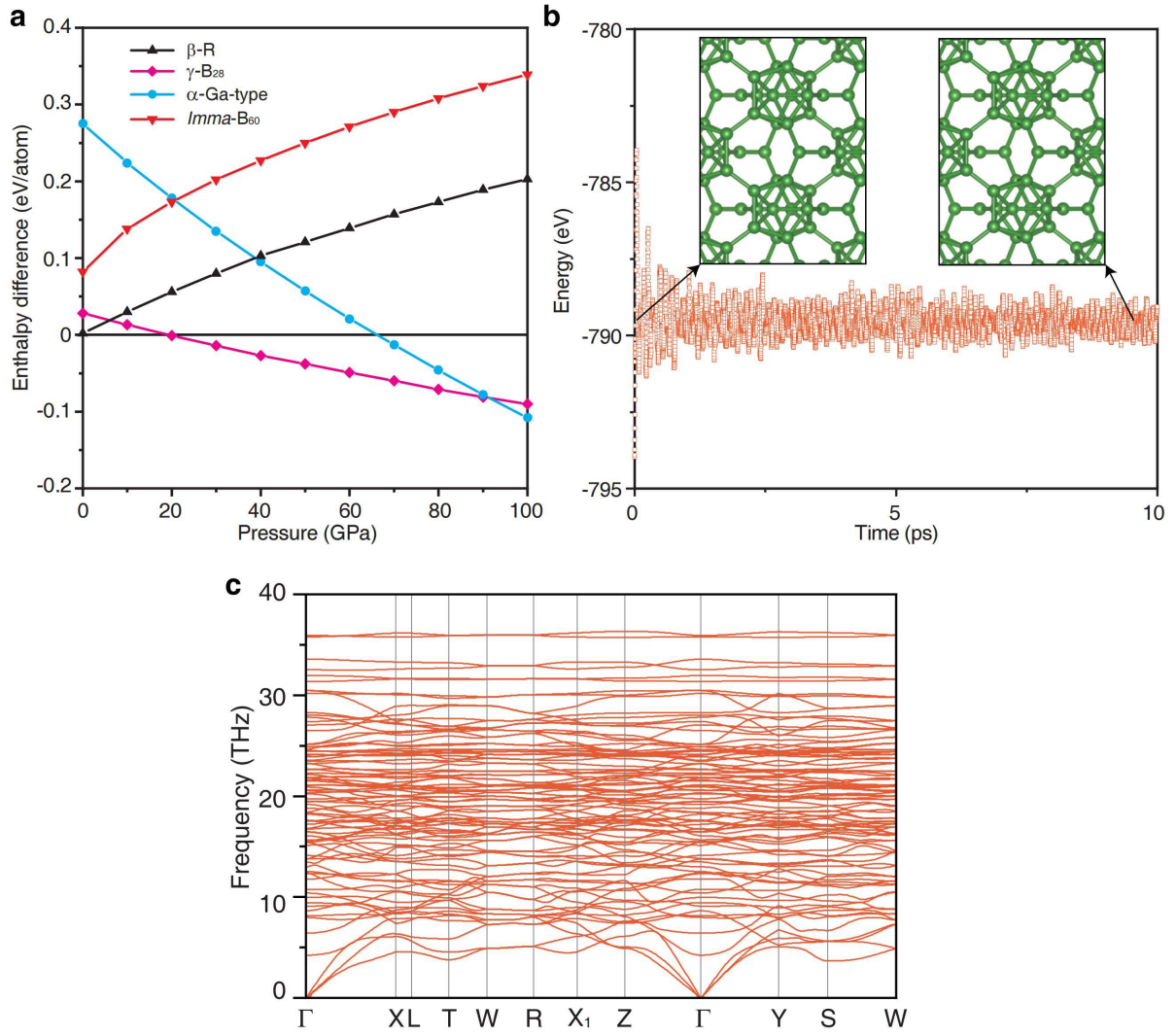
Atom	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ¹²	<i>U</i> ¹³	<i>U</i> ²³
B1	0.0063	0.0028	0.0042	-0.0008	0.0011	-0.0007
B2	0.0047	0.0039	0.0047	0.0007	-0.0003	-0.0004
B3	0.0063	0.0026	0.0097	0.000	0.000	-0.0014
B4	0.0055	0.0029	0.0044	0.000	0.000	0.0013
B5	0.0151	0.0051	0.0108	0.000	0.000	-0.0039
B6	0.52	0.029	0.022	0.000	0.000	0.000
Na	0.0164	0.0078	0.0074	0.000	0.000	0.000

4. Elemental analysis for B₆₀ via EDS to determine residual Na content



Supplementary Fig. 1 | Large-area EDS analysis of degassed B₆₀. **a**, Representative EDS spectrum of the synthesized B₆₀. Weak C and O signals arise from the conductive tape used for sample mounting. **b**, SEM image of powdered B₆₀ (350 μm × 240 μm). **c,d**, Corresponding EDS elemental mapping of B and Na, respectively. The residual Na content is as low as 0.08 at% by EDS, comparable to background levels, confirming the nearly complete removal of sodium in B₆₀ samples.

5. Thermodynamic and dynamic stability of *Imma*-B₆₀



Supplementary Fig. 2 | Thermodynamic and dynamic stability of *Imma*-B₆₀. **a**, Enthalpies of *Imma*-B₆₀ and other boron phases relative to α -R, indicating *Imma*-B₆₀ as a metastable phase across the studied pressure range. **b**, Energy evolution of a 2×1×1 supercell of *Imma*-B₆₀ structure during an NVT molecular dynamics simulation at 0 GPa and 300 K. No irreversible energy drift is observed beyond thermal fluctuations. Insets show the initial and final structures, confirming no structural collapse or major distortion. **c**, Calculated phonon dispersion, which shows no imaginary frequencies throughout the first Brillouin zone, confirming dynamic stability.

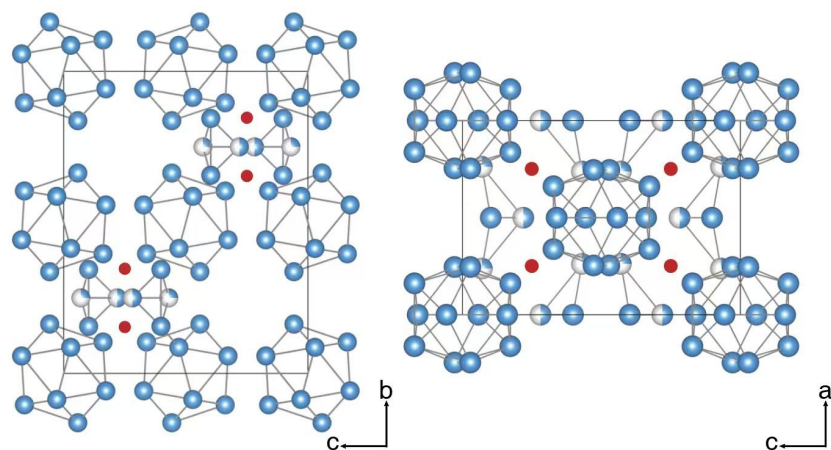
6. Microcrystal electron diffraction (MicroED) of *Imma*-B₆₀

Supplementary Table 5 | Fractional atomic coordinates and occupancy of *Imma*-B₆₀ determined from MicroED data.

atom	x	y	z	Occ.
B1	0.2460(20)	0.0863(16)	0.0285(14)	1
B2	0.1620(14)	0.0578(17)	0.8275(13)	1
B3	0.0000	0.1040(30)	0.1610(20)	1
B4	0.0000	0.1633(18)	0.9425(17)	1
B5	0.0000	0.1560(20)	0.3980(20)	1
B6-1	0.0000	0.2500	0.2810(70)	0.5
B6-2	0.2380(90)	0.2500	0.0700(60)	0.25

Supplementary Table 6 | Structure refinement parameters based on the MicroED data.

Crystal data	
Chemical formula	B ₆₀
Crystal system	orthorhombic
Space group	<i>Imma</i>
<i>a</i> , <i>b</i> , <i>c</i> /Å	5.8000(12), 10.2800(17), 8.3200(20)
<i>α</i> , <i>β</i> , <i>γ</i> /°	90, 90, 90
<i>V</i> /Å ³	496.07(18)
<i>Z</i>	1
Intensity measurement	
Diffractionmeter	Talos F200S
<i>T</i> _{meas} /K	293(2)
Radiation	Electron (<i>λ</i> = 0.02508 Å)
Scan mode	Continuous Rotation
Time per step /s	0.1
<i>θ</i> range /°	0.222 to 2.15
Refinement of the structure	
No. measured reflections	1496
No. unique reflections	281
No. reflections used in refinement	281
No. parameters used in refinement	22
Reflection range	-7 ≤ <i>h</i> ≤ 7, -10 ≤ <i>k</i> ≤ 10, -12 ≤ <i>l</i> ≤ 12
<i>R</i> _{int}	0.2290
<i>R</i> (<i>σ</i>)	0.4915
Final <i>R</i> indices (<i>F</i> _{obs} > 4 <i>σ</i> (<i>F</i> _{obs}))	<i>R</i> ₁ = 0.1465, <i>ωR</i> ₂ = 0.3914
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2284, <i>ωR</i> ₂ = 0.4387
Δ <i>ρ</i> _{max} , Δ <i>ρ</i> _{min} (e Å ⁻³)	0.24, -0.18
Goodness of fit	1.117



Supplementary Fig. 3 | Crystal structure of B₆₀ determined from MicroED. Residual density attributed to B₆-associated defects is marked in red.

7. Structural comparison between *Imma*-B₆₀ and other synthesized boron allotropes

Supplementary Table 7 | Structural parameters of the as-synthesized B₆₀ and previously reported boron allotropes.

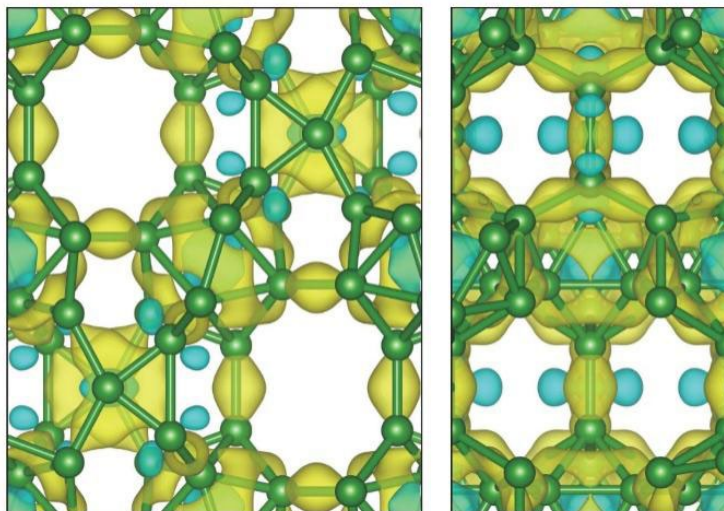
Structure	Symmetry	Lattice parameter (Å)	Atoms per cell	Density (g/cm ³)	Interstitial units	Refs
<i>Imma</i>-B₆₀	<i>Imma</i>	a=5.8054 b=10.2802 c=8.3258	60	2.168	Triangular B ₃	This work
<i>α</i>-R	<i>R-3m</i>	a=5.057 α=58.06°	12	2.467	None	Decker et al. ⁵
<i>β</i>-R	<i>R-3m</i>	a=10.145 α=65.17°	~105	2.322	Single B atom	Hoard et al. ⁶
<i>γ</i>-B₂₈	<i>Pnnm</i>	a=5.0316 b=5.5997 c=6.9388	28	2.571	B ₂	Oganov et al. ⁷
<i>ε</i>-B₁₅	<i>R-3m</i>	a=5.2278 α=67.45°	15	2.299	Linear B ₃	Parakhonskiy et al. ⁸
<i>ζ</i>-B₈	<i>Cmce</i>	a=2.939 b=5.330 c=3.260	8	2.812	--	Chuvashova et al. ⁹
<i>α</i>-T₅₂	<i>P4₂/nnm</i>	a=b=8.75 c=5.06	52	2.410	Single B atom	Hoard et al. ¹⁰
<i>δ</i>-T₅₀	<i>P4₂/nnm</i>	a=b=8.708 c=5.075	50	2.332	Single B atom	Parakhonskiy et al. ⁸
<i>pc</i>-T₅₂	<i>P4₂/nnm</i>	a=b=8.293 c=5.863	52	2.315	Single B atom	Kurakevych et al. ¹¹
<i>δ</i>-O_{51.5-52}	<i>Pnnn</i>	a=8.894 b=8.7843 c=5.0189	51.5-52	2.381	Single B atom	Ekimov et al. ¹²
<i>β</i>-T₁₉₂	<i>P4₃</i>	a=b=10.14 c=14.17	~192	2.366	Single B atom	Vlasse et al. ¹³

8. Chemical bonding analysis of *Imma*-B₆₀

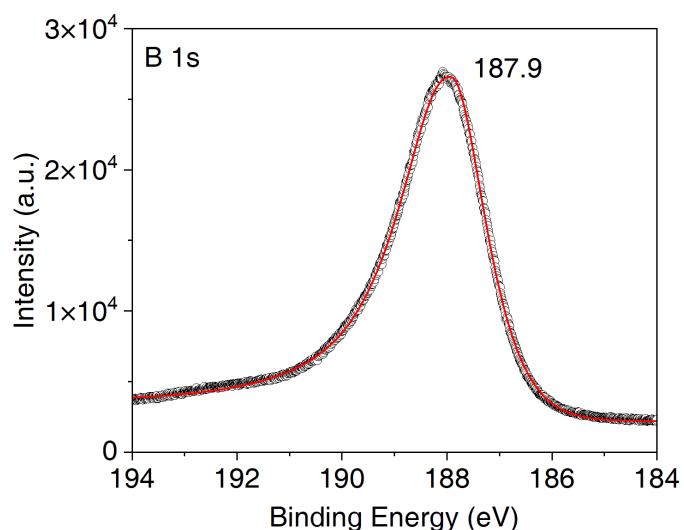
Multicenter bonding analysis on *Imma*-B₆₀ and *Imma*-Na₄B₆₀ was performed using Solid State Adaptive Natural Density Partitioning (SSAdNDP)¹⁴. The analysis reveals a complex network of multicenter bonds in *Imma*-B₆₀. The orthorhombic unit cell contains 180 valence electrons. Following Wade's rule for closo-structures¹⁵, the four B₁₂ icosahedra account for $2 \times 13 \times 4 = 104$ electrons for intra-icosahedral bonding, leaving 76 electrons for the inter-cluster framework. This bonding scheme comprises a combination of localized and delocalized multicenter bonds (Extended Data Fig. 7), including: i) four three-center-two-electron (3c-2e) bonds within the four interstitial B₃ units (B5-B5-B6), ii) twelve 2c-2e bonds interconnecting the B₁₂ icosahedra (four B4-B4 and eight B2-B2), iii) eight 3c-2e bonds linking the B₁₂ icosahedra to the B₃ units (B3-B5-B6); iv) sixteen 2c-2e bonds between the B₁₂ icosahedra and the B₃ units (B1-B5). Full occupation of this network requires 80 electrons, exceeding the 76 electrons available in B₆₀. Consequently, several bonds, particularly the sixteen B1-B5 bonds, are partially occupied, with an occupation number (ON) of only 1.73|e|. This electron deficiency introduces states near the Fermi level, explaining the observed metallic behavior of *Imma*-B₆₀ (Extended Data Fig. 8d). In the case of *Imma*-Na₄B₆₀ precursor, donation of four electrons from Na fully occupies the B1-B5 bonds (ON=1.85|e|), resulting in a semiconducting state with a closed-shell electron count of 184 electrons (Extended Data Fig. 8c). The covalent network formed by bonds within the interstitial B₃ units and those linking them to the B₁₂ icosahedra establishes a distinct structural architecture, differentiating *Imma*-B₆₀ from other boron allotropes. This analysis underscores the importance of synthesizing the more electronically stable semiconducting precursor.

Charge distribution in *Imma*-B₆₀ was analyzed by calculating its deformation charge density, defined as the difference between the total charge density of the crystal ($\rho(\text{B}_{60})$) and the superposition of isolated, not-interacting B_i boron atoms ($\rho(\text{B}_i)$), $\rho(\text{B}_{60}) - \sum_{i=1}^{60} \rho(\text{B}_i)$. The resulting map reveals how electron density redistributes upon bonding. As illustrated in Supplementary Fig. 4, electron density accumulates primarily in the regions between two or three bonded atoms, while depleting in out-of-plane directions. This pattern, along with the head-to-head overlap of wavefunctions visible in the Extended Data Fig. 7, indicates that σ -

type bonding dominates throughout the system. Importantly, all five characteristic bond types identified in the earlier SSAdNDP analysis are clearly distinguishable in the deformation charge density visualization, confirming the consistency between these two complementary bonding-analysis approaches.



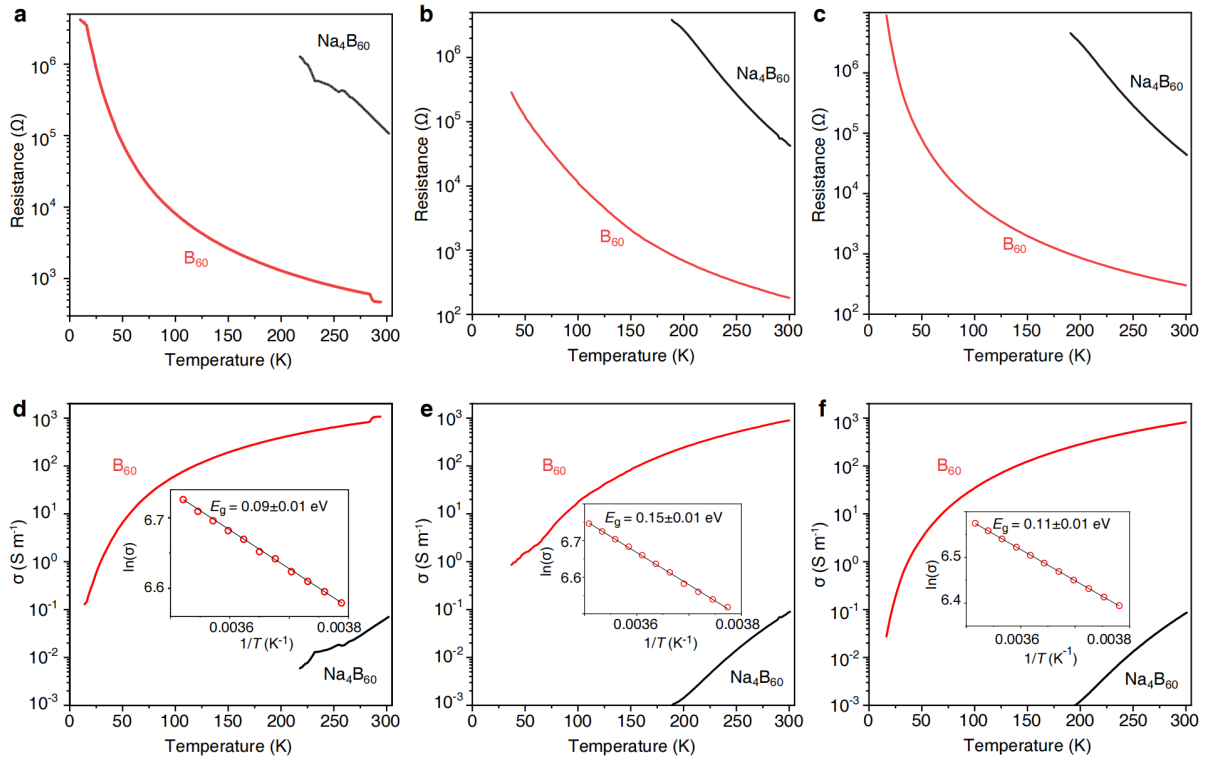
Supplementary Fig. 4 | Deformation charge density of *Imma-B*₆₀. The deformation density is superimposed on the crystal structure and shown along the [100] and [001] directions. Yellow and blue isosurfaces indicate electron accumulation and depletion, respectively.



Supplementary Fig. 5 | B 1s XPS spectra of *Imma-B*₆₀.

9. Electronic transport properties of Na₄B₆₀ and B₆₀

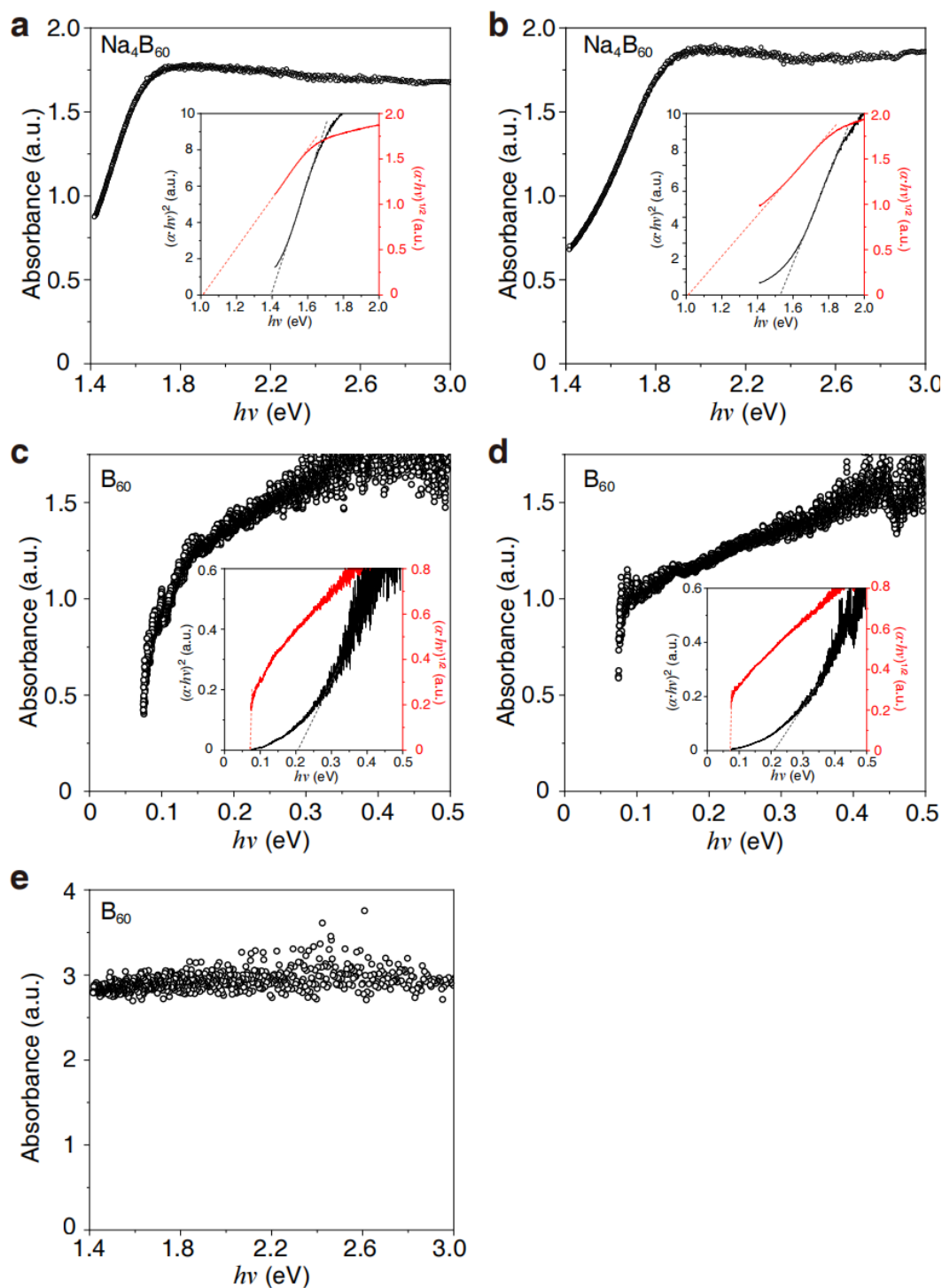
Temperature-dependent resistance measurements were performed on three independent Na₄B₆₀ and B₆₀ samples, respectively. A sharp reduction in resistance by two to three orders of magnitude was observed after degassing process (Supplementary Fig. 6a–c). Based on the measured thicknesses of 1–2 μm for B₆₀, the conductivities from three independent measurements are $(10.7 \pm 3.6) \times 10^2$, $(9.0 \pm 3.0) \times 10^2$, and $(8.2 \pm 2.7) \times 10^2$ S m⁻¹, yielding an average value of $(9.1 \pm 1.8) \times 10^2$ S m⁻¹, which is four orders of magnitude higher than the average conductivity of Na₄B₆₀, $(8.2 \pm 1.0) \times 10^{-2}$ S m⁻¹ (thickness 80–110 μm). Using the Arrhenius plot (Supplementary Fig. 6d–f), the electrical bandgap of B₆₀ was estimated to be 0.09 ± 0.01 , 0.15 ± 0.01 and 0.11 ± 0.01 eV from the three independent measurements, yielding an average value of 0.12 ± 0.01 eV.



Supplementary Fig. 6 | Temperature-dependent electrical transport of B₆₀ and Na₄B₆₀. **a–c**, Temperature-dependent resistance of Na₄B₆₀ and B₆₀ from three independently prepared samples. **d–f**, Corresponding temperature-dependent conductivity converted from the resistance data in **a–c**, respectively. Insets show Arrhenius plots ($\ln(\sigma)$ versus $1/T$) used to extract the bandgap.

Supplementary Table 8 | Room-temperature electrical conductivity and bandgap of B₆₀ in comparison with representative boron phases.

Phase	Conductivity (S m ⁻¹)	Band gap (eV)	Ref.
B ₆₀	$(9.1 \pm 1.8) \times 10^2$	0.21 (direct) 0.07 (indirect)	this work
α -R		2.0, 2.4	Horn et al. ¹⁶ , Franz et al. ¹⁷
β -R	$\sim 1 \times 10^{-5}$	1.56	Werheit et al. ^{18,19}
γ -B ₂₈	$\sim 1 \times 10^{-4}$	1.9	Zarechnaya et al. ²⁰
α -T ₅₂	1.7×10^{-4}	1.55	William et al. ²¹
boron carbide(B _{4.3} C, B _{6.4} C, B _{7.91} C, B _{8.52} C, B _{10.37} C)	$1 \times 10^2 \sim 1 \times 10^3$	2.09, 2. 41	Werheit et al. ^{22–24} , Kuhlmann et al. ²⁵

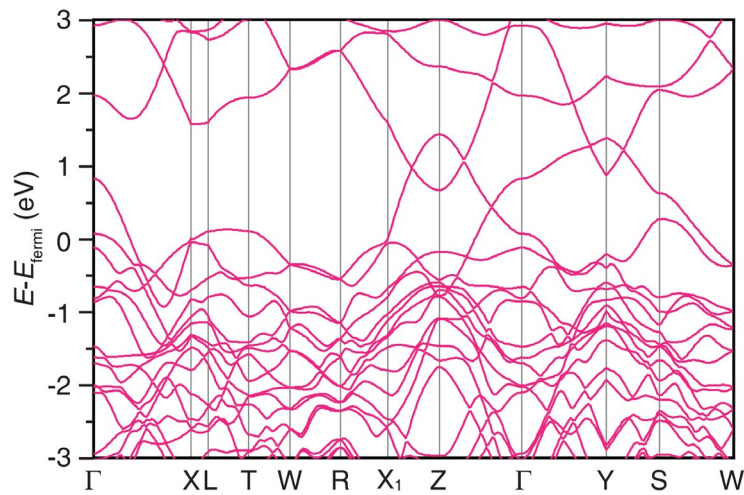


185

186 **Supplementary Fig. 7 | Optical adsorption of Na₄B₆₀ and B₆₀.** a,b, Two additional
 187 independent UV-Vis absorption spectra of Na₄B₆₀ measured under the same conditions as in
 188 Fig. 3b. c,d, Two additional independent IR absorption spectra of B₆₀ measured under the same
 189 conditions as in Fig. 3c. e, UV-Vis absorption spectrum of B₆₀.

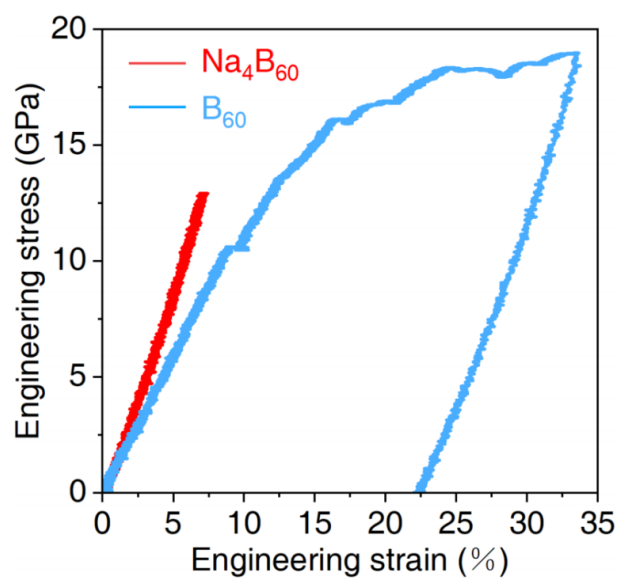
11. Calculated band structures of *Imma*-Na₄B₆₀ and *Imma*-B₆₀

The band structures of *Imma*-Na₄B₆₀ *Imma*-B₆₀ was initially calculated using the GGA-PBE functional, which predicted a typical semi-metallic and metallic behavior, respectively (Extended Data Fig. 8a,b). Considering the known underestimation of PBE functional, we further carried out electronic structure calculations using the hybrid HSE06 functional (via PWMAT^{26–28}) and GW quasiparticle corrections (GW₀-PBE via VASP2 and WANNIER90 interface^{29,30}). For ideal *Imma*-Na₄B₆₀, HSE06 does open a band gap of 0.5 eV (Extended Data Fig. 8c), which remains smaller than the experimentally measured indirect bandgap of 1.04 eV. Notably, in the case of ideal *Imma*-B₆₀, neither HSE06 nor GW₀ succeeded in opening a discernible bandgap (Extended Data Fig. 8d and Supplementary Fig. 8). A significant finding emerges when we instead employed the defect-containing structures (identified via XRD in Extended Data Fig. 5) for calculations. A bandgap of 1.44 eV (indirect) and 0.23 eV (indirect) opens for *Imma*-Na₄B₆₀ (Extended Data Fig. 8e) and *Imma*-B₆₀ (Extended Data Fig. 8f), respectively. We would like to note that while these calculated values are comparable to the experimental measurements, the simulations are based on simplified periodic models containing a single defect type. Real crystals feature a multitype of randomly distributed defects, a complexity beyond the scope of our current DFT treatment. Nevertheless, these results strongly suggest that the presence of defects likely explains the inconsistency between the electronic structure of actual samples and that predicted for the ideal structures.



Supplementary Fig. 8 | Band structure of the ideal *Imma*-B₆₀ crystal calculated using the GW₀ correction.

213 **12. In-situ uniaxial compression data of B₆₀ and Na₄B₆₀**



214

215 **Supplementary Fig. 9 | Replicated in-situ uniaxial compression along [010] of B₆₀ and**
216 **Na₄B₆₀ nanopillars.**

217

Reference:

1. Tang, W., Sanville, E. & Henkelman, G. A grid-based Bader analysis algorithm without lattice bias. *J. Phys.: Condens. Matter* **21**, 084204 (2009).
2. Okamoto, H. Supplemental literature review of binary phase diagrams: B-La, B-Zn, Bi-La, Bi-Ti, Cd-Pr, Ce-Ga, Cu-Na, Ge-Ta, Ge-Y, H-Zr, Na-Si, and Pb-Sc. *J. Phase Equilib. Diff.* **36**, 644–655 (2015).
3. Pelton, A. D. The Na-Zn (Sodium-Zinc) system. *Bull. of Alloy Phase Diagrams* **8**, 550–553 (1987).
4. Albert, B. et al. “NaB₁₅”: A new structural description based on X-ray and neutron diffraction, electron microscopy, and solid-state NMR spectroscopy. *Chem. Eur. J.* **6**, 2531–2536 (2000).
5. Decker, B. F. & Kasper, J. S. The crystal structure of a simple rhombohedral form of boron. *Acta Crystallogr.* **12**, 503–506 (1959).
6. Hoard, J. L., Sullenger, D. B., Kennard, C. H. L. & Hughes, R. E. The structure analysis of β -rhombohedral boron. *J. Solid State Chem.* **1**, 268–277 (1970).
7. Oganov, A. R. et al. Ionic high-pressure form of elemental boron. *Nature* **457**, 863–867 (2009).
8. Parakhonskiy, G., Dubrovinskaia, N., Bykova, E., Wirth, R. & Dubrovinsky, L. High pressure synthesis and investigation of single crystals of metastable boron phases. *High Pressure Res.* **33**, 673–683 (2013).
9. Chuvashova, I. et al. Nonicosahedral boron allotrope synthesized at high pressure and high temperature. *Phys. Rev. B* **95**, 180102 (2017).
10. Hoard, J. L., Hughes, R. E. & Sands, D. E. The structure of tetragonal boron. *J. Am. Chem. Soc.* **80**, 4507–4515 (1958).
11. Kurakevych, O. O. & Solozhenko, V. L. Crystal structure of dense pseudo-cubic boron allotrope, pc-B₅₂, by powder X-ray diffraction. *J. Superhard Mater.* **35**, 60–63 (2013).
12. Ekimov, E. A. et al. A new orthorhombic boron phase B_{51.5–52} obtained by dehydrogenation of “ α -tetragonal boron”. *J. Mater. Res.* **31**, 2773–2779 (2016).
13. Vlasse, M., Naslain, R., Kasper, J. S. & Ploog, K. Crystal structure of tetragonal boron related to α -AlB₁₂. *J. Solid State Chem.* **28**, 289–301 (1979).

14. Galeev, T. R., Dunnington, B. D., Schmidt, J. R. & Boldyrev, A. I. Solid state adaptive natural density partitioning: a tool for deciphering multi-center bonding in periodic systems. *Phys. Chem. Chem. Phys.* **15**, 5022–5029 (2013).
15. Wade, K. The structural significance of the number of skeletal bonding electron-pairs in carboranes, the higher boranes and borane anions, and various transition-metal carbonyl cluster compounds. *J. Chem. Soc., Chem. Commun.* 792–793 (1971).
16. Horn, F. H. Some Electrical and Optical Properties of Simple Rhombohedral Boron. *J. Appl. Phys.* **30**, 1611–1612 (1959).
17. Terauchi, M., Kawamata, Y., Tanaka, M., Takeda, M. & Kimura, K. Electron Energy-Loss Spectroscopy Study of the Electronic Structure of α -Rhombohedral Boron. *J. Solid State Chem.* **133**, 156–159 (1997).
18. Werheit, H. *Die Halbleitereigenschaften des Bors*. In: Madelung, O. (eds) Festkörperprobleme 10. Advances in Solid State Physics, vol 10. Springer Berlin Heidelberg (1970).
19. Werheit, H. & Leis, H. G. On the conductivity mechanism of β -rhombohedral boron. *Phys. Status Solidi B* **41**, 247–253 (1970).
20. Zarechnaya, E. Y. et al. Superhard semiconducting optically transparent high pressure phase of boron. *Phys. Rev. Lett.* **102**, 185501 (2009).
21. Shaw, W. C., Hudson, D. E. & Danielson, G. C. Electrical Properties of Boron Single Crystals. *Phys. Rev.* **107**, 419–427 (1957).
22. Werheit, H. Structural defects: essential elements of icosahedral boron-rich solids. *Sustain. Ind. Process. Summit* **8**, 159 (2015).
23. Werheit, H. Are there bipolarons in icosahedral boron-rich solids? *J. Phys.: Condens. Matter* **19**, 186207 (2007).
24. Werheit, H. & Kuhlmann, U. Superconductivity in boron carbide? Clarification by low-temperature MIR/FIR spectra. *J. Phys.: Condens. Matter* **23**, 435501 (2011).
25. Kuhlmann, U. & Werheit, H. On the microstructure of boron carbide. *Solid State Commun.* **83**, 849–852 (1992).
26. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **118**, 8207–8215 (2003).

27. Krukau, A. V., Vydrov, O. A., Izmaylov, A. F. & Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **125**, 224106 (2006).
28. Jia, W. et al. Fast plane wave density functional theory molecular dynamics calculations on multi-GPU machines. *J. Comput. Phys.* **251**, 102–115 (2013).
29. Fuchs, F., Furthmüller, J., Bechstedt, F., Shishkin, M. & Kresse, G. Quasiparticle band structure based on a generalized Kohn-Sham scheme. *Phys. Rev. B* **76**, 115109 (2007).
30. Mostofi, A. A. et al. wannier90: A tool for obtaining maximally-localised Wannier functions. *Comput. Phys. Commun.* **178**, 685–699 (2008).